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SYNTHESIS OF OPTICALLY UNIFORM GLASSES CONTAINING GOLD NANOPARTICLES: SPECTRAL AND NONLINEAR OPTICAL PROPERTIES

V. I. Savinkov,[1] G. Yu. Shakhgil'dyan,[1, 2] A. Paleari,[1] and V. N. Sigaev[1, 3]

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A method for preparing batches, melting, producing and modifying the structure of phosphate glass on a nanoscale by introducing gold nanoparticles were developed. Samples of glass with different content of phosphorus oxide were synthesized. The samples were heat-treated in a gradient furnace. Their physical, spectral and nonlinear optical properties were studied.

Key words: phosphate glass, gold nanoparticles, absorption spectrum, nonlinear optical properties.

The coloring of glasses by colloidal solutions of metals, specifically, gold, has been known since ancient times. However, right up to the end of the 19th century colored glasses were used exclusively for household and decorative purpose [1]. In the first half of the 20th century there was a burst of interest in systems containing metal nanoparticles, which led to the systematization of the data on coloring of glass by ions and colloidal colorants. Thus, after the ultramicroscopic work by R. A. Zsigmondy and G. Seidentopf (1903 – 1919) the nature of the coloring of gold ruby became clear [2] and the study of colloidal solutions of gold established analogies between the absorption spectra of solutions and glasses colored with gold. The x-ray diffraction study of gold ruby glasses confirmed the presence of metallic gold in glasses [3].

Using the G. Tamman's theory of crystallization of supercooled liquids R. A. Zsigmondy explained the process leading to the formation of colloidal gold particles in glass. Thus, during glassmaking gold salts dissociate at high temperature, then metallic gold dissolves in the molten glass without the formation of chemical compounds, and metallic gold is present in a molecular-disperse state in the solution and does not color the glass. At temperatures below the production temperature the glass becomes supersaturated with gold because the solubility of gold decreases and it can recrystallize out. On cooling the glass colored by gold becomes colorless, and a red region appears only with repeated heating to the softening temperature, when the glass acquires a certain mobility and the dissolved gold precipitates on existing crystalline centers, forming colloidal particles that can be distinguished with the aid of an electron microscopy and color the glass in a red color, which is characteristic of colloidal gold solutions.

Subsequent studies of gold ruby glasses, performed by Lange, Bankcroft, Garnet and Sil'verman using more accurate methods of determining particle sizes, established a relation between the size, shape and number of colloidal particles and spectral characteristics of glasses. Thus, it was determined that glass with an intense liver color contains particles at least 56 nm in diameter, while the diameter of particles contained in samples of transparent glasses is much shorter. For 70 – 100 nm gold particles there are indications of opacification in the glass, while the main functions of 200 – 500 nm particles are reflection and scattering of light. In general, the color carriers in glass are 5 – 60 nm crystals, colorless or light-yellow glasses obtain with crystals smaller than 5 nm, rose colored glass with 10 nm, violet-red hues with 10 – 20 nm and, finally, 20 – 50 nm particles make it possible to obtain red or purple ruby [4]. Obtaining gold ruby by introducing gold chloride, which is obtained by dissolving metallic gold in a mixture of concentration hydrochloric and nitric acids, into glass has been well studied by domestic specialists but only in application to artistic articles made from colored glass [5].

At the same time the metal nanoparticles described above have been intensively studied in nonlinear optics for the last 20 years because of their unique optical properties. Nanoparticles of metals such as copper, silver and gold have a wide absorption band in the visible range. The absorption by such nanoparticles is associated with the phenomenon of surface plasma resonance (SPR), which arises when the sur-

[1] D. I. Mendeleev Russian Chemical Technology University, Moscow, Russia.
[2] E-mail: georgiy.shahgildyan@gmail.com.
[3] E-mail: vlad.sigaev@gmail.com.

face plasma impulses equal the vector components of the photon impulse parallel to the reflection plane. The properties of localized plasmons depend directly on the shape of the nanoparticles, which makes it possible to tune their resonance system to the effective interaction with light or elementary quantum systems [6]. It has been shown that high values of the third-order nonlinear susceptibility $\chi^{(3)}$ are reached in media with gold inclusions, as a result of which the nonlinear response of the nanoparticles is strongest under the conditions of resonance excitation of free electrons in them, specifically, at the SPR frequencies [7 – 9].

In summary, because of the good prospects for creating optical switches with an ultrashort response and optical limiters based on the particulars of nonlinear absorption materials containing metal nanoparticles are of interest for use in different fields — in nonlinear optics, laser physics and opto-electronics. A key question in developing such materials is the choice of matrix, which must be an ideal medium for nonlinear processes and meet prescribed technological and economic requirements. The criterion of quality and value of the material for use in superfast, completely optical systems is a high ratio $n_2/\tau\alpha$, where n_2 is the nonlinear index of refraction, τ is the nonlinear response time and α is the absorption coefficient.

Thus, even though oxide glasses have low n_2 compared with other materials, their high transparency and low response losses make them promising media for creating such devices.

The nonlinear refractive index n_2 depends strongly on the composition of the glass and in oxide glasses it varies over two orders of magnitude from 2.7×10^{-20} m^2/W for SiO_2 composition to 1.3×10^{-18} m^2/W for glass in the system PbO–BiO_3–GeO_2. The value of n_2 is directly related with the nonlinear polarizability (hyperpolarizability) of the bonds in the structure of the glass, and for this reason glasses containing highly polarizable cations of atoms such as Ti, Bi, Tl, Pb and a number of other transition and rare-earth elements exhibit the strongest nonlinearity. The cubic nonlinearity in fluoride glass is on the whole weaker than in oxide glass and, conversely, stronger in chalcogenide glass. The quantity $\chi^{(3)}$ increases sharply when oxide glasses are doped with semiconductor crystals or nano-size metal particles.

In a number of cases, when self-focusing of a beam must be avoided, glass with the lowest possible value of n_2 is required. This is especially important when the glass is used as a base for the active medium in high-power lasers or serves as a channel for the propagation of an intense flux of light. Undesirable self-focusing can result in improper operation or damage to the optical setup. The lowest values of n_2 have been found in fluoroberyllate glasses ($n_2 = 7.5 \times 10^{-21}$ m^2/W), but because of the high toxicity of beryllium compounds and the difficult of fabrication they are not produced for commercial purposes. Second in line is quartz glass ($n_2 = 2.7 \times 10^{-20}$ m^2/W), but it is difficult to obtain an active medium with the required characteristics on its basis.

One of the most practicable solutions is to use a phosphate matrix possessing a nonlinear index of refraction of the order of 3×10^{-20} m^2/W, chemical stability, mechanical strength and convenient production characteristics. In the present work we present the results of the synthesis of a series of modified phosphate glasses containing gold nanoparticles and the properties of these glasses.

Modified phosphate optical glass, developed at D. I. Mendeleev Russian Chemical Technology University, was chosen as the matrix of the glass [10]. Tin oxide SnO_2 was introduced into the glass by substituting for P_2O_5 to prevent segregation of gold nanoparticles at the melting stage and production of the molten glass. This glass, designated as P-60, contains the following (mol.%): 59.49 P_2O_5, 13.82 K_2O, 10.74 BaO, 8.45 Al_2O_3, 4.80 B_2O_5, 2.38 SiO_2 and 1.02 SnO_2. Samples with different molar ratio P_2O_5/K_2O (55/19 and 65/9) designated as P-55 and P-65 were also synthesized. Sol with gold nanoparticles was prepared by a procedure developed separately.

Weighed portions of hydrogen tetrachloroaurate ($HAuCl_4 \cdot 4H_2O$) and glutathione were added to a mixture of methyl alcohol and distilled water with constant mixing. Next, 0.2M sodium borohydride solution was introduced into the solution, after which the color of the reaction mixture changed to dark-brown. The mixture obtained was let standing for one day. The precipitate formed was separated by decantation, centrifuged, dried and dissolved in water. The size distribution of the gold particles in the solution was determined using a Zetasizer Nano ZS (Malvern) (measurement range 0.6 – 6000 nm) by means of dynamic light scattering (radiation wavelength 633 nm). The average particle size was found to be 1.87 nm. The prepared sol with mass content 0.01% Au was introduced into the glass above 100%. A feature of the batch preparation was that the prepared dry part of the batch was mixed with sol and evaporated in a muffle furnace at temperature 125°C in 1 h to formation of a uniform dry mass. Then the prepared dry part was mixed with a computed amount of orthophosphoric acid, adding the dry part of the charge in small portions during mixing.

The glass was made in a laboratory electric furnace, with SiC by heaters, in a 100 ml quartz vessel with enough charge for 100 g of glass. The liquid charge was loaded into a heated crucible in portions, not allowing the material to foam or overflow. Melting was conducted at 1400°C, the molten glass was transferred into a heated mold, after which the casting was annealed in a muffle furnace at 400°C for 4 h and allowed to cool to 30°C.

The nonisothermal crystallization of massive glass samples was studied by differential thermal analysis (DTA) using a Netzsch STA 449 apparatus in a regime with temperature increasing evenly at the rate 10 K/min to 1200°C. X-ray phase analysis of powders of the glasses obtained was performed in a Bruker D2 Phaser diffraction tool. The density of

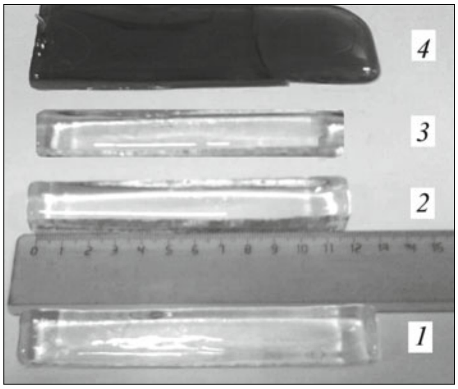

Fig. 1. Phosphate glass castings: *1*) without gold nanoparticles (P-60 matrix); *2*, *3*) containing 0.01% gold nanoparticles (compositions P-65 and P-60, respectively); *4*) with gold, introduced via $HAuCl_4 \cdot 4H_2O$ (composition P-60).

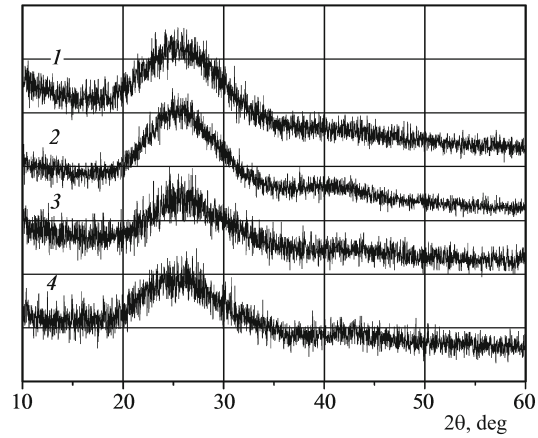

Fig. 2. Results of XPA of powders of the synthesized glass samples: *1*) P-60 matrix; *2*, *3*, and *4*) P-65, P-60 and P-55 with gold nanoparticles.

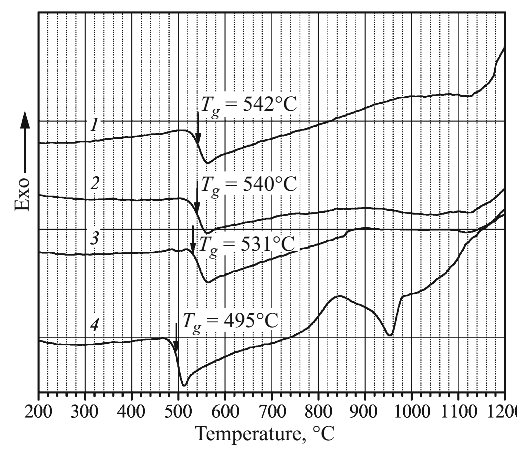

Fig. 3. Results of DTA of the synthesized glass samples: *1*, *2*, *3*, and *4*) same as in Fig. 2.

the glasses, measured by hydrostatic weighing in water using a YDK 01 densitometer for the Sartorius GC 803S-OCE scales, varied from 2.7333 to 2.7375 g/cm^3. The surface of the samples obtained was analyzed using a Bruker Artax x-ray spectral analyzer. TEM analysis of the samples and electronic diffraction analysis of the powders of the glasses obtained were performed with a FEI Tecnai G2 F20 microscope with accelerating voltage 200 kV. The optical absorption of the glass samples was studied with a Varian Cary 50 spectrophotometer.

The glass samples obtained with mass content of Au nanoparticles 0.01% were colorless after rough annealing and there were no indications of crystallization, just as for the samples of Au-free glass. The synthesis of the glasses with similar compositions but containing an equivalent volume of gold, introduced into the glass matrix directly via $HAuCl_4 \cdot 4H_2O$, resulted in intense coloring of the molten glass even at the glass melting stage (Fig. 1). It is obvious that this method of introducing metals into a glass matrix does not give the desired results with respect to spectral characteristics.

The XPA results are displayed in Fig. 2. There are no sharp peaks in the x-ray diffraction pattern, which attests to an amorphous structure of the synthesized glasses, while the crystalline inclusions are so small that they cannot by detected even in intensely colored samples.

The DTA curves of monolithic samples of the glasses obtained are presented in Fig. 3. As the content of the alkali component K_2O in the glasses increased the temperature T_g decreased in the interval from 540 to 495°C. The DTA curve for the sample with the composition P-55 contains a sharp exothermal peak at temperature of the order of 840°C. The data obtained show that the composition of the glass matrix plays a large role when gold particles are introduced, especially considering the fact that this sample with composition with elevated alkali component content had a liver color even at the production stage. The increase of the vitrification temperature with increasing P_2O_5 content is associated with an increase of the connectedness of the anionic motif of the matrix of the phosphate glass. The differential-thermal analysis agrees well with the theory of the structure of phosphate laser glasses [11].

Subsequent heat-treatment in a gradient furnace at temperatures below T_g was performed on the colorless glass samples with gold. The results demonstrated the change in the color of the glass samples from colorless to red (Fig. 4). As a result it is possible to determine the heat-treatment regimes (temperature and duration) required to obtain glass samples with the required spectral characteristic in combination with the required nonlinear spectral parameters.

The results of electron microscopy (EM) of a heat-treated sample of glass with the composition P-60 are presented in Fig. 5. The results of high-resolution EM in the colored part of the sample demonstrate the formation of spherical gold particles no larger than 10 nm with a monocrys-

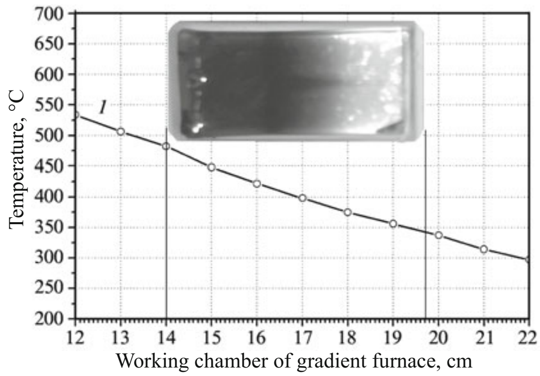

Fig. 4. Parameters of a gradient furnace with heat-treated phosphate glass sample with composition P-60, containing 0.01% gold nanoparticles: *1*) temperature of movable thermocouple.

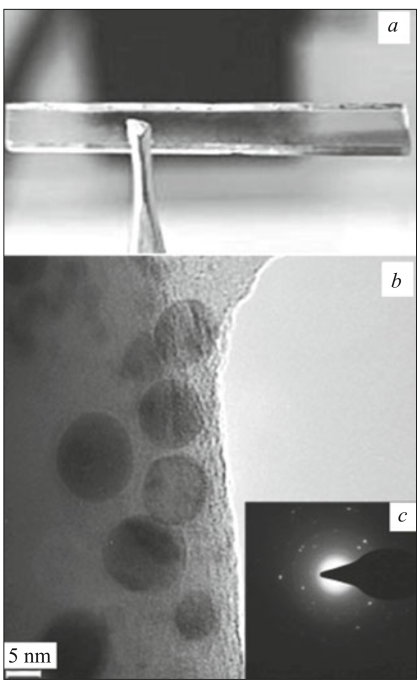

Fig. 5. Investigation of glass samples with the composition P-60: *a*) overall view of the sample; *b*) image from the electron microscope of the structure of the sample in the heat-treated zone; *c*) diffraction pattern of the sample in the heat-treated zone.

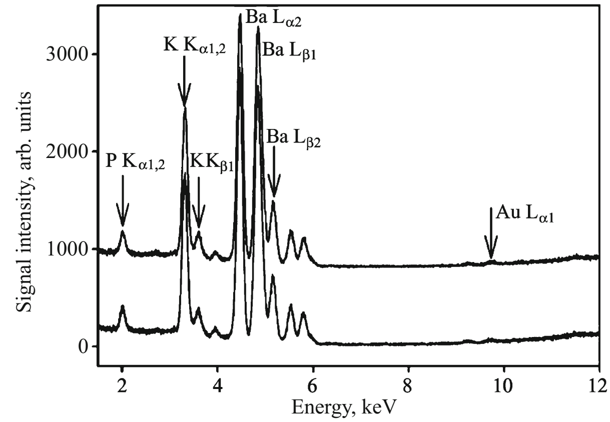

Fig. 6. Spectra from x-ray fluorescence analysis of a glass sample with the composition P-60 in colored (*a*) and colorless (*b*) sections, located at different distances from the sample edge — 0 mm (0.11 ± 0.02) and 20 mm (0.12 ± 0.02), respectively.

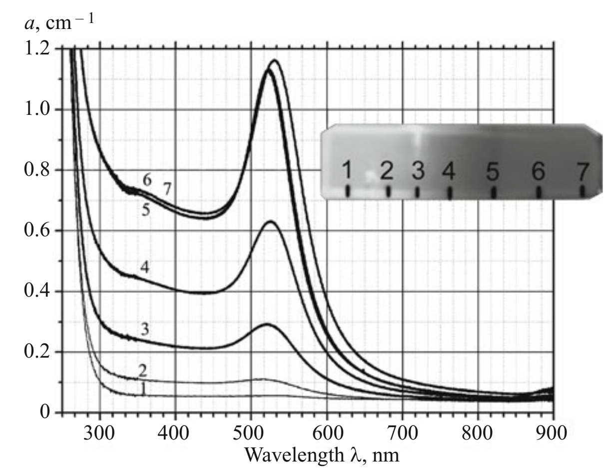

Fig. 7. Spectral curves of the absorption α of heat-treated in a gradient furnace sample of P-60 glass (the numbers indicate the points of spectrum recording).

talline structure, well determined by the atomic structure and the crystal lattice constant of gold.

It is important to note that x-ray fluorescence analysis of the sample of heat-treated glass with the composition P-60 in the direction of the heat-temperature gradient (Fig. 6) fixes the constant value of the gold concentration in the glass (together with other components of the glass). This confirms a homogeneous distribution of gold in the glass matrix and elucidates the change in the spectral characteristics associated with the growth of gold crystals on the nanoscale.

A strict relation between the observed color and growth of gold nanoparticles with increasing heat-treatment temperature was found along the entire length of the sample successively from point to point by recording the optical absorption spectrum (Fig. 7). We note that analysis of the recorded absorption spectrum makes it possible to fix the characteristic response which must be associated to the SPR phenomenon in gold in the visible range spectrum near 520 nm. The difference of the maximum absorption values from the position of the measurement point is associated with the increase and decay of the SPR. A detailed study of the spectra in this region showed that as the nanoparticles increase in size on the initial section the peak shifts in the direction of lower energy values of the increase in the absorption intensity, while on the final section of the increase in the absorption intensity

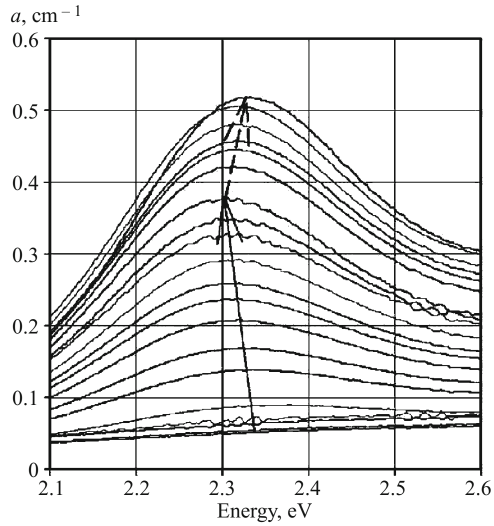

Fig. 8. Spectral curves of the absorption of heat-treated in a gradient furnace sample of P-60 glass (the arrows indicate the shift of the SPR).

the maximum of the peak rapidly returns in the direction of higher energy (Fig. 8).

The nonlinear optical processes associated with self-focusing and self-defocusing in materials were studied using the highly sensitive single-beam method of Z scanning by the well-known procedure described in [12], with whose help the nonlinear index of refraction, nonlinear susceptibility and nonlinear absorption coefficient are determined. This method is based on the study of the change in the intensity profile of a Gaussian beam in the far zone as the sample moves along the Z axis in the focusing region. Z-Scanning of a heat-treated sample of glass with the P-60 composition containing gold particles was performed according to two schemes — with closed and open diaphragm. The results are presented in Fig. 9.

Preliminary analysis of the results of Z-scanning using the scheme with a closed diaphragm showed that both sections of the sample (colored and colorless) possess measurable values of the nonlinear absorption coefficient. At the same time the nonlinear absorption in the colored section of the sample is much stronger than in the colorless section. More detailed interpretation of the results of Z-scanning, calculation of the nonlinear refractive indices and nonlinear susceptibilities as well as measurements performed on samples with other compositions are subjects for future research.

As a result a procedure was developed for preparing charges, melting, production and modification of the structure of phosphate glass on the nanoscale by introducing gold particles. It was shown that the composition chosen for the glass and the procedure developed for synthesis make it possible to introduce a large quantity of gold into the glass while preserving the lack of color, which can be used in industry to obtain nonlinear optical elements. The conditions for controllable formation of gold nanoparticles in a phosphate glass matrix were determined. The spectral and nonlinear optical properties of samples of the glasses obtained with different heat-treatment regimes were studied. The presence of sharp nonlinear optical effects in the glass samples obtained was confirmed experimentally. The glass samples obtained are excellent precursors for studying and developing methods of controlled local formation of gold nanoparticles in oxide glass by laser radiation and for studying their effect on the nonlinear optical characteristics.

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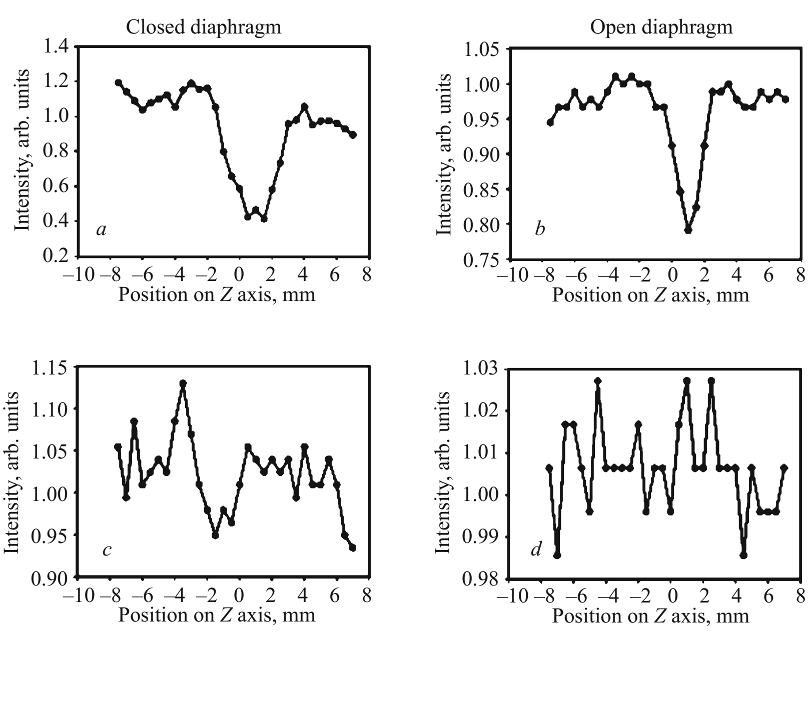

Fig. 9. Z-Scanning results for a glass sample with composition P-60, containing gold nanoparticles with open and closed diaphragm: *a* and *b*) in the colored region of the sample; *c* and *d*) in the colorless region of the sample.

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